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APPLICATION OF A HOT WIRE IONIZATION DETECTOR TO AUTOMOTIVE EXHAUST GAS ANALYSIS

TO

U. S. Public Health Service
Department of Health, Education & Welfare

Attention: Dr. Aubrey P. Altshuller, Project Officer

Contract No: PH 86-66-117

BY

Micro Tek Instruments Corporation
Baton Rouge, Louisiana

Date: March 17, 1967

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Date: March 17, 1967

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PREFACE & SUMMARY

The objective of this work has been to investigate the application of a catalytic combustion ionization detector to the determination of hydrocarbons in automotive exhaust. The catalytic element is a coiled platinum hot wire of the general type used in conventional catalytic combustion detector cells in which thermal effects are measured. In the present device the effect measured is the ion current resulting from charged radicals formed during the process of catalytic combustion.

A major feature of this technique for auto exhaust gas analysis is its complete selectivity to C_2+ hydrocarbons in the presence of CO, H_2, CH_4, CO_2, air and H_2O.

This study examines the effect of operating parameters on selectivity to different types of hydrocarbons, results are compared to those obtained with the Flame Ionization Detector, and typical results on actual auto exhaust samples are reported.

It is concluded that the CCID* can be a critical component in a composite "black box" analyzer to be used for field surveillance of automobile exhaust with regard to emission of hydrocarbons and carbon monoxide.

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*Catalytic Combustion Ionization Detector

I. INTRODUCTION

Progress Report No. 1 (11-3-66) discussed preliminary results in a relatively large reaction chamber in which the catalytic surface was a cylindrical platinum foil. The objective with that apparatus was to make fundamental kinetic investigations under conditions where the reaction temperature could be accurately measured and controlled. It was not anticipated that that apparatus would serve as a prototype for a detector cell for field use.

Although work reported in Progress Report No. 1 indicated the feasibility of total hydrocarbon analysis by measurement of ions created during catalytic combustion (without interference from carbon monoxide), difficulties were encountered with high standing current levels emitted from the platinum foil. Therefore all tests and studies conducted during the later phases of the project were made using a different detector cell described herein.

A. Discussion of Basic Approach

Figure I shows a schematic diagram of the apparatus used to obtain all data presented in this Final Report. The Catalytic Combustion Ionization Detector -- hereinafter referred to as "CCID" -- is shown in cross-section in Figure II.

It may be observed in Figure I that samples were not flowed on a continuous basis through the CCID cell. Rather, compressed air was continually flowed through the cell and samples were injected as "pulses" by means of a 7-port gas sampling valve inserted in the air flow line. The amount of sample injected was determined by the size of the sample loop on the injector valve.

This pulse sampling technique is considered to be an important feature of the methods developed. The detector is essentially mass responsive. Therefore, the "peak height" of detector response to sample pulses is dependent upon the carrier air flow rate. On the other hand the area under the peak should be relatively independent of the air flow rate. This fact, in a finally designed auto exhaust gas analyzer, would permit use of an integral (area) output which would be independent of flow variations. In such an apparatus sample size is easily reproduced by means of the sampling valve which would receive the sample at a nominal pressure of one atmosphere.

Figure I also indicates that tests comparing the CCID to a Flame Ionization Detector (FID) were conducted with the FID in series with the CCID.

* * * *

It is pertinent to call attention to prior work which has been conducted at the U. S. Naval Research Laboratories on "A Study of the Ionization Produced By the Catalytic Combustion of Hydrocarbons". This work by Umstead et al* presents data of immediate interest in connection with the possible application of the catalytic combustion ionization technique to exhaust gas analysis. One objective of the present study was to confirm the work of Umstead and to examine more exhaustively the kinetic aspects of the catalytic reactions. For instance, in limited data Umstead and co-workers found little or no effect of space velocity over the catalytic filament, which is surprising from an elementary theoretical point of view. Also, the temperatures at which he found maximum ion responses appeared to be high (ca. 750-800°C), in fact several hundred degrees higher than the temperatures at which he observed high combustion conversions.

The detector cell used in the present work, as seen in Figure II, differs from that of Umstead primarily by virtue of its lower volume and geometry wherein the catalytic coil is mounted on the axis of the reaction cavity. These design features were intended to assure high gas-catalyst contacting efficiency and to minimize by-passing over a reasonable range of flow rates.

It is believed that in the present work ion production and combustion conversions were limited primarily by the usual controlling kinetic parameters, i.e. temperature and space velocity.

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*UMSTEAD, M. E., WOODS, F. J., and JOHNSON, J. E., Journal of Catalysis: Volume 5, 293-300 (1966)

SCHEMATIC OF AUTO EXHAUST ANALYZER

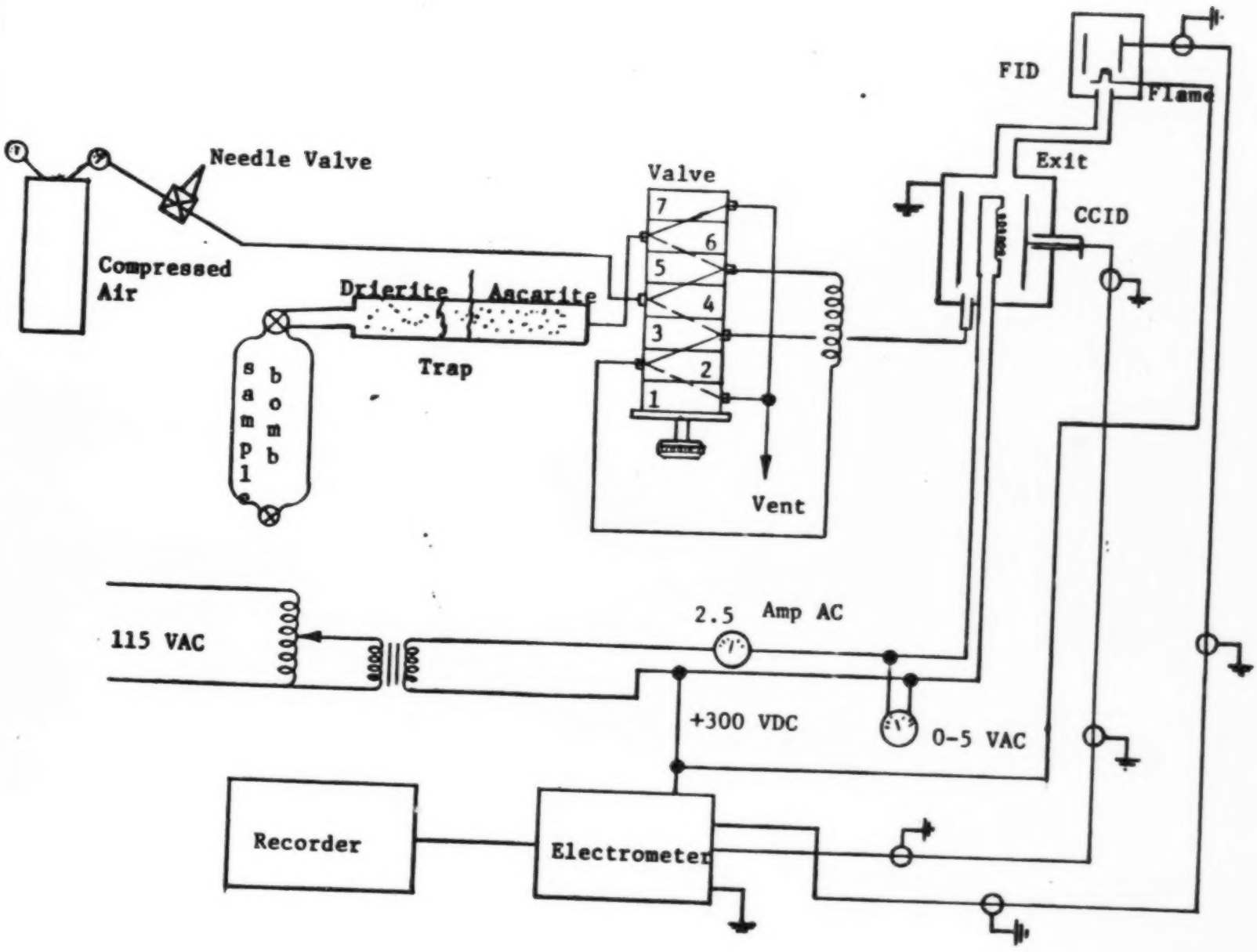


FIG. 1

SECTION DRAWING OF CCI DETECTOR CELL

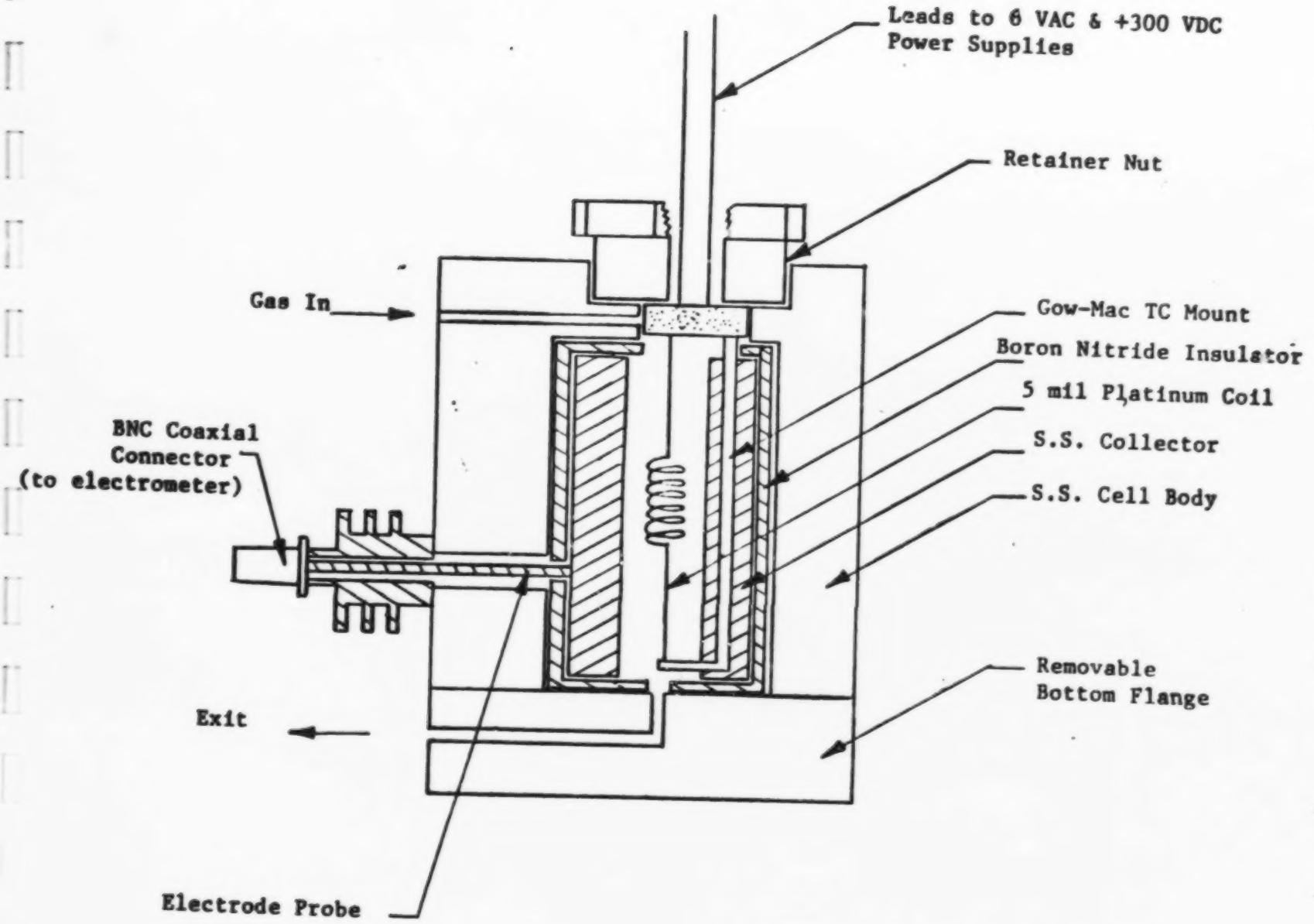


FIG. II

B. Description of Apparatus and Procedures

- CCID Detector Cell

Figure II is a diagram of the detector used in this investigation. The platinum coil dimensions are 0.005"D x 2". The wire was coiled around a 1/16" dia. cylinder to produce 6 convolutions and spot welded between the posts of a standard Gow-Mac T.C. Filament Holder. The coil was positioned with the cell as shown in Figure II. The internal detector volume was 0.104 milliters.

- Flame Ionization Detector (FID)

The flame detector used in this investigation to compare response with the CCID is shown in Figure I. The flame tip was polarized + 300 VDC above ground potential. The flame tip diameter was 0.02". The hydrogen flow rate was held constant at 50 ml/minute while the air flow was maintained at 600 ml/minute. For this investigation the sample gas flow into the detector from the exit of CCID was in the range of 12 to 60 cc/min.

- Electronics

The heating current for the platinum filament was supplied by a 115 volt AC variable auto transformer, the output of which was stepped down to 0-6.3 VAC by means of a filament transformer. No attempt was made to regulate this simple filament power source.

A Micro Tek Model 636800 Electrometer with an integral 300 VDC power supply was used to measure ion currents and to supply polarizing voltage to the CCID and FID.

- Recorder

The recorder used was a type H Leeds & Northrup, 1 mv Full Scale, chart speed 1/3" per minute.

- Sample Valve

A Micro Tek Model 713207 7-port linear sampling valve was used to introduce the samples into the detector. For these studies sample loop sizes were 15 and 30 ML.

- Drierite-Ascarite Trap

  A 60 cm x 4 mm. stainless steel tube was plumbed between the sample bomb and the 7-port valve. One-half of the tube was filled with drierite and the other with ascarite. The drierite section was connected to the bomb.

- Carrier Gas

  The Carrier Gas was air (Big 3 Company, Houston, Texas). Flow was adjusted with a 10 turn stainless steel Nupro needle valve. Periodic checks during the day were made to assure the correct flow was maintained for each experiment. Flow measurements were made by means of a bubble meter.

- Hydrocarbon Standards

  1. Methane - Mathison Co.
  2. Ethylene - Mathison Co.
  3. Butane - Mathison Co.
  4. 2,2-dimethylbutane - Phillips
  5. Benzene
  6. Hexane
  7. Acetylene
  8. Simulated auto exhaust: (Prepared by Scott Research Laboratory, Inc. Perkasie, Pa.)

Methane	4000 ppm	Iso-butylene	1000 ppm
Ethane	200 ppm	Acetylene	1000 ppm
Butane	200 ppm	Benzene	400 ppm
Pentane	200 ppm	Toluene	1000 ppm
Hexane	150 ppm		
Ethylene	2500 ppm		
Propylene	1000 ppm	TOTAL:	12,050 ppm in nitrogen

- Sample Preparation

  The simulated auto exhaust, methane, butane, ethylene and acetylene samples were prepared by evacuating a 1700 ml bomb and then filling the bomb with the appropriate gas and finally pressurizing the bomb with air to the desired dilution.

  The hydrocarbon samples which were liquid at room temperature were introduced into an evacuated bomb with a Hamilton 10 ul syringe. The bomb was then pressurized with air to the desired dilution.

- Collection and Preparation of Auto Exhaust Samples

A 200 ml bomb was evacuated to 30 mm Hg. A 4 mm o.d. x 21 cm long S. S. probe connected to the entrance of the bomb was extended its full length into the tailpipes. A needle valve connecting the probe to the bomb was opened for 1 minute and then closed. The bomb was finally pressurized to 45 psi with air.

- Temperature Calibration of the Catalytic Combustion Platinum Filament

The resistance of the filament was measured at room temperature. Next the filament was positioned inside a Temco Muffle Furnace oven and heated slowly to 1000°C. As the temperature increased, periodic measurements were made to determine the change of resistance of the filament. Separately, with the filament mounted in the cell at 40°C, the relationship between filament current and resistance was established. Cross plotting of the data from the two experiments yielded the calibration curve of Figure III.

This method of calibration relates the average filament temperature to the filament current. It is presumed that temperatures at the center of the filament could be of the order of 100°C higher than at either end of the wire.

TEMPERATURE CALIBRATION OF FILAMENT

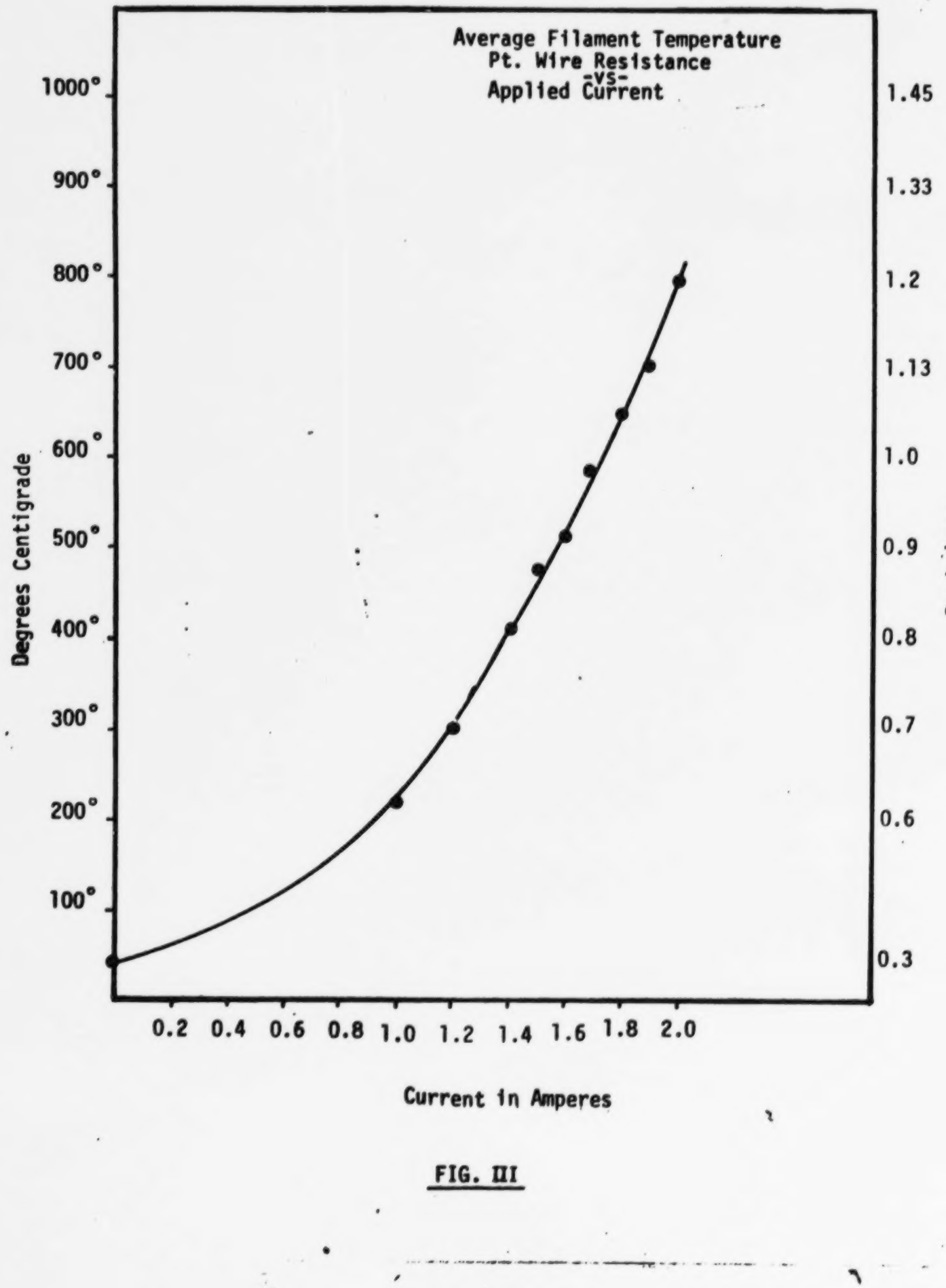


FIG. III

II. DISCUSSION OF RESULTS

A. Examination of Background Signal

As reported in Progress Report No. 1, there is always some measurable positive ion background signal obtained from the hot platinum coil with pure air passing over it. No success was achieved in activating and cleaning the large platinum surfaces on the foil used in the apparatus described in Progress Report No. 1.

Experience with the platinum coil wire filament used in the present study duplicated that of Umstead. In general it was found that:

- Negative polarization of the coil produced higher standing currents. Therefore, the preferred practice was to use positive polarization.

- The platinum surface could be quickly cleaned and standing current reduced by operating the coil at higher currents and temperatures for brief periods of 10 to 60 seconds.

- Figure IV shows the effect of filament current and temperature on standing current. The filament currents of less than 1.8 amperes (approx. 660°C) produced standing currents low enough (ca. less than 10^{-11} amps) to obtain favorable signal to noise ratios for hydrocarbon sample concentrations in the range of 10 to 1,000 ppm.

- Although standing currents did not generally increase with filament exposure to multiple samples, periodic "flashing" or "regeneration" of the filament was adopted as a standard procedure to maintain catalytic activity.

B. Effect of Operating Parameters

- Form of Recorded Data

  Figure V shows a typical recorded response of the CCI detector to pulse sampling injections. It is encouraging to note the absence of serious "tailing" on the backside of the peaks. Because of the square wave form of the response, it was possible to multiply peak heights by peak widths to obtain coulometric (area) responses.

CCID Background Ion Current
-vs-
Filament Current and Temperature

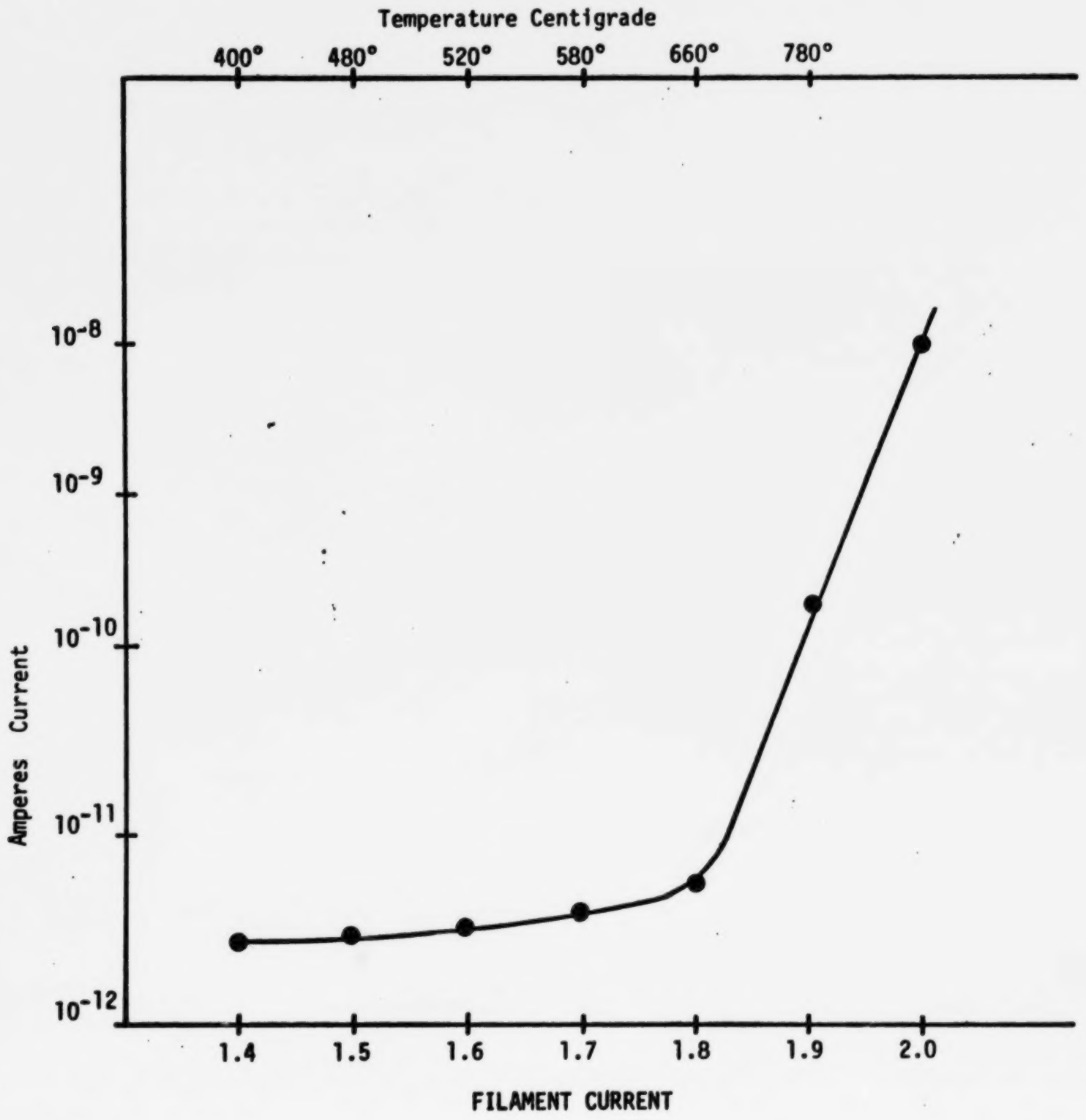
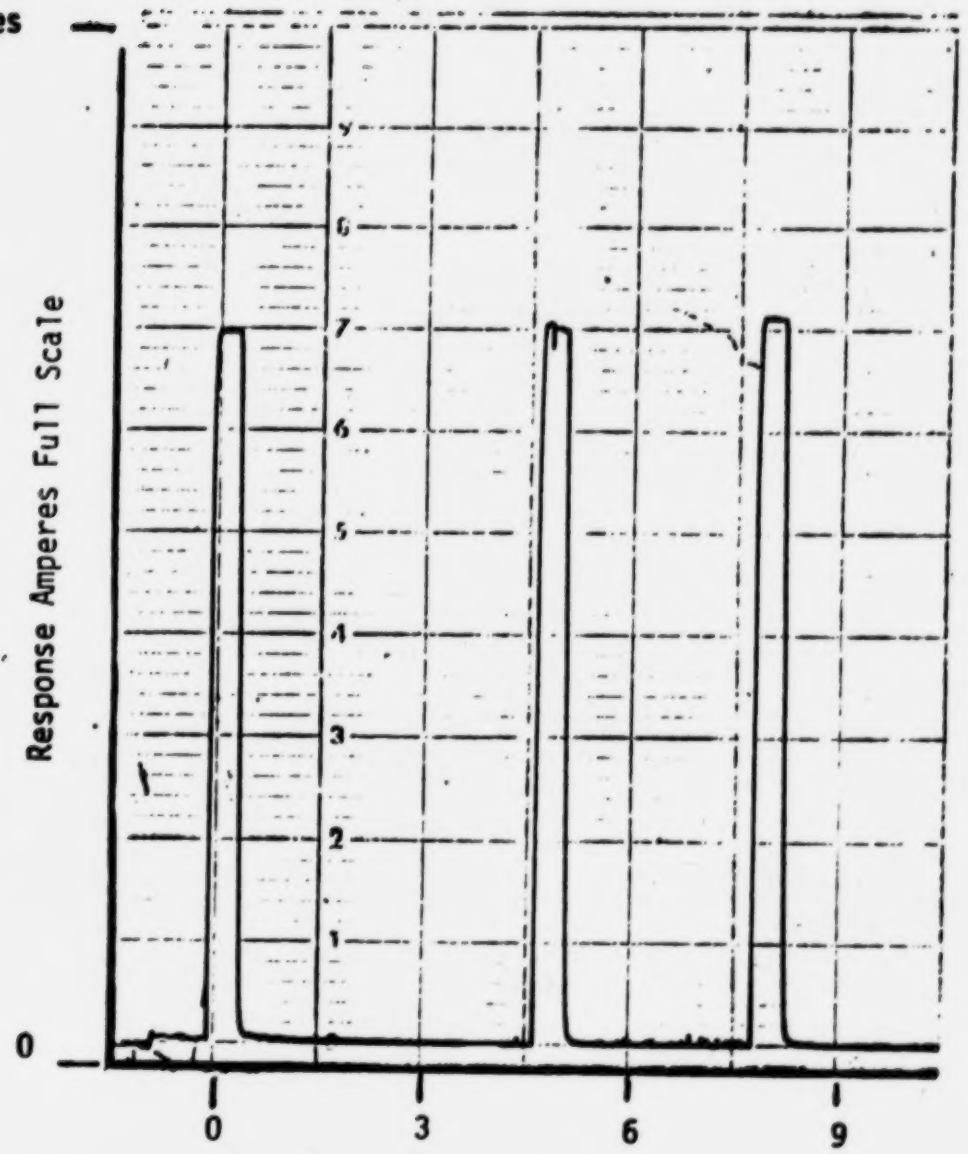


FIG. IV

RESPONSE OF CCI DETECTOR

To Triplicate Sample Pulses of 2,2-dimethylbutane In Air



Analytical Conditions:

Sample: 0.025% 2,2-dimethylbutane in air
Sample size: 30 ml (Pulse Technique)
Detector: CCID
Flow Rate: 24 ml/minute
Applied Current: 1.6 amperes
Electrometer Setting: 3.2×10^{-9} amperes full scale
Chart Speed: 13"/minute
Recorder: L&N Model H (1 MV full scale)

FIG. V

- Effect of Temperature on Response to Hydrocarbons

Figure VI shows the expected effect of temperature on response to typical hydrocarbons. The response maxima are in the temperature range of 500 to 700°C. This is 100 to 200 degrees lower than Umstead observed for maximum ion production. Umstead's filament temperatures were measured with an optical pyrometer which probably gave temperature readings corresponding to the brightest or hottest center portion of the platinum coil. Temperatures reported in these studies are based on measurement of coil resistance, which provides for an imputed "average" wire temperature. This could account in large measure for the difference between these results and those of Umstead.

A further possibility concerning the temperature at which ionization begins and the temperature at which maximum ionization occurs is that the reaction cell of the present work was designed with kinetic considerations in mind. It seems probable that the present cell would give higher conversions at lower temperatures than would the cell used in Umstead's work because of lower space velocities and better gas-catalyst contacting.

The high response of the CCI detector to 2,2-DMB is consistent with Umstead's observation about branched compounds and is consistent with the theoretical considerations concerning the ease of fragmentation of branched hydrocarbons.

- Effect of Flow Rate

Figure VII shows the effect of flow rate on response to 0.08 percent normal butane in air. The detector shows an increase in peak height (amperometric) response with increased flow rate of the sample pulse across the filament. This is expected since the detector should be, as is the hydrogen flame detector, a mass sensitive device. The leveling off of amperometric response at flow rates above 30 cc's per minute suggests that the space velocity is too high for higher flow rates and that catalyst by-passing is occurring.

If the detector can indeed be operated in a mass responsive mode, then there should be no effect of flow rate on the peak area which is the coulometric response. Table I confirms that the detector is mass sensitive and exhibits the expected constant coulometric response with varying flow rate over a wide range of flow and sample concentrations.

EFFECT OF CURRENT (Temperature) ON RESPONSE
OF VARIOUS TYPES OF HYDROCARBONS

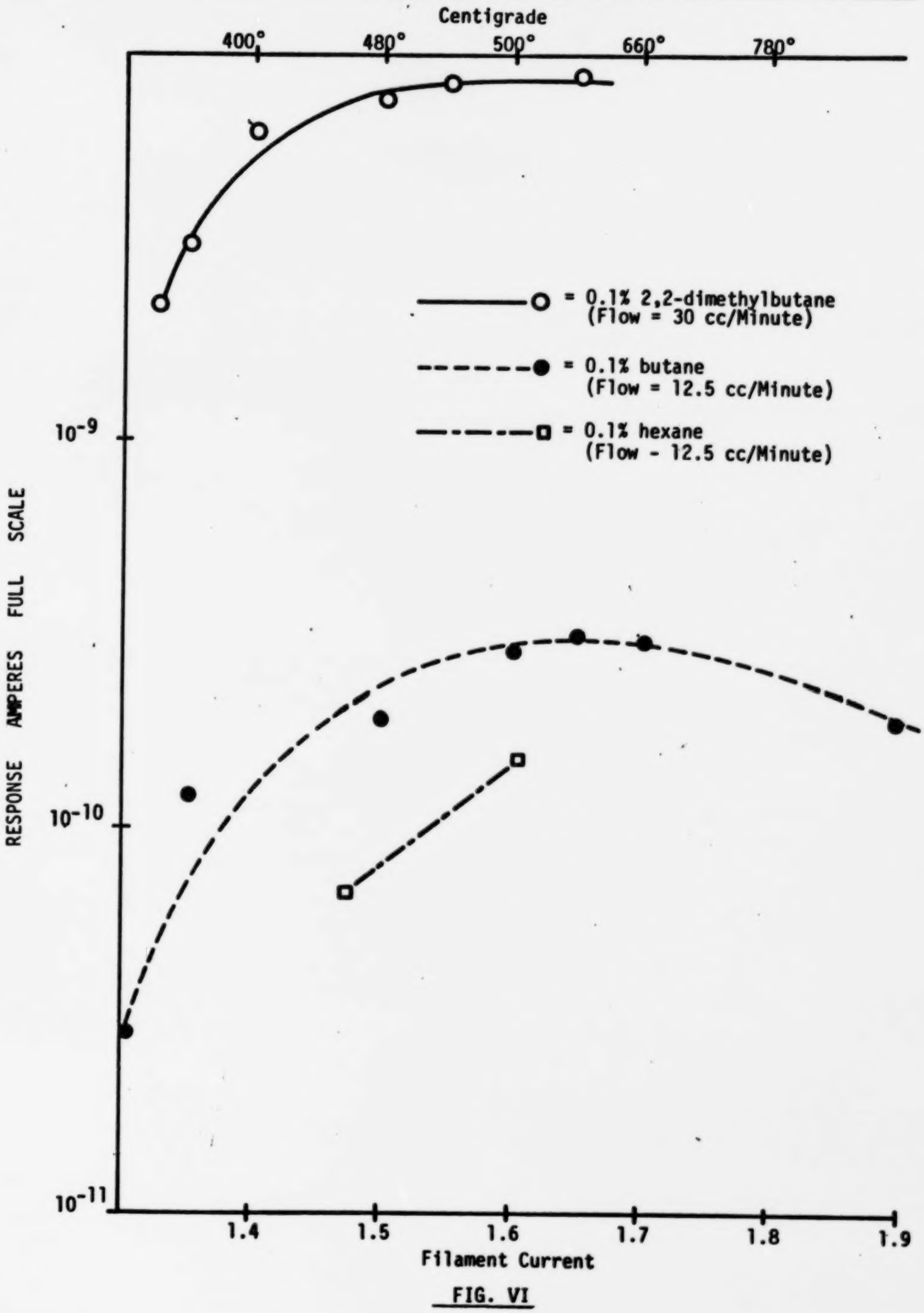


FIG. VI

Effect of Flow Rate On Response of CCI Detector

o = I_f = 1.6 amperes
x = I_f = 1.5 amperes
Sample: 0.08% butane in air

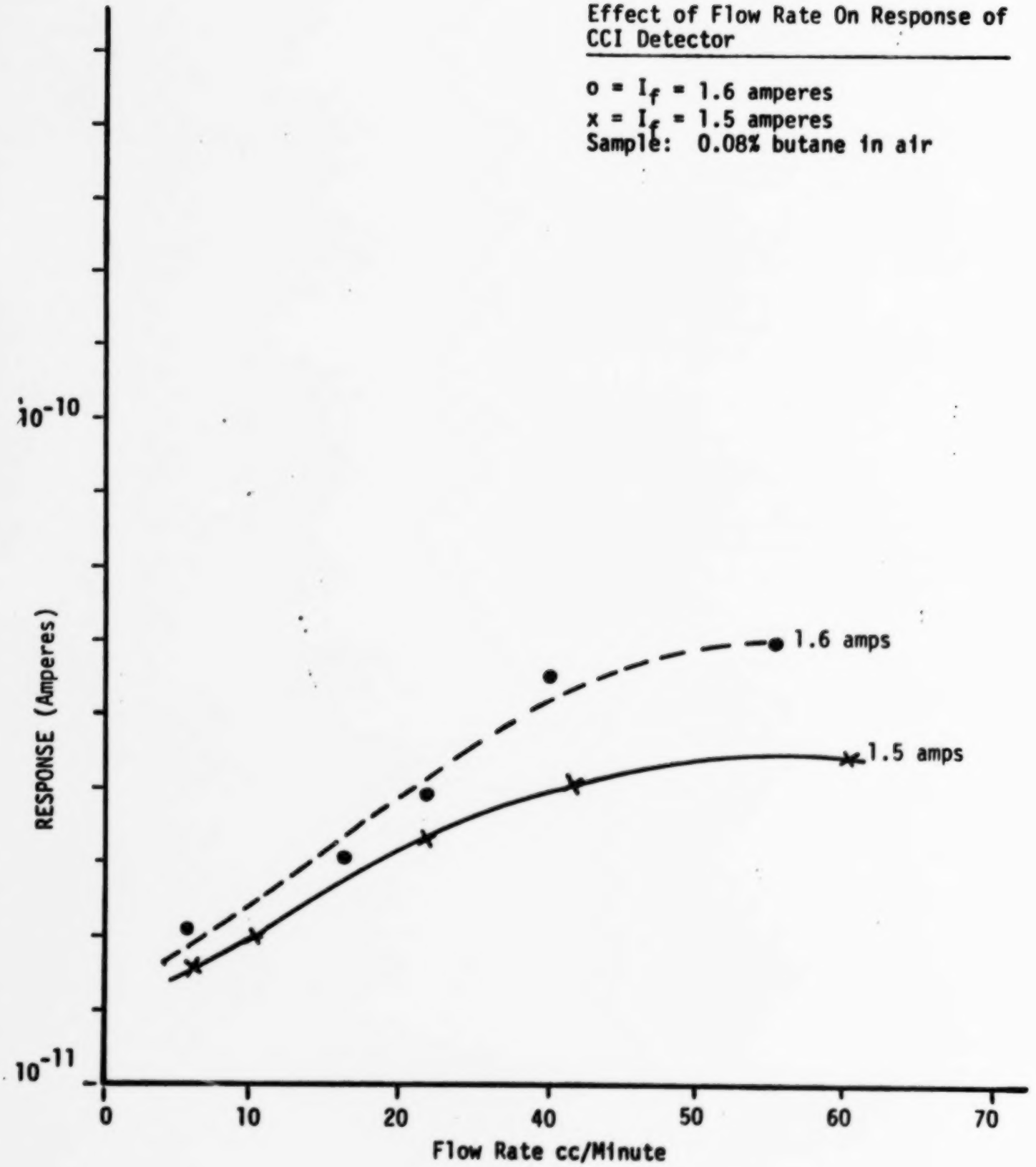


FIG. VII

TABLE I

EFFECT OF FLOW RATE ON COULOMETRIC RESPONSE

CCI DETECTOR RESPONSE TO 0.16% BUTANE IN AIR (*)

FLOW RATE IN CC/MINUTE	PEAK HEIGHT AT 8 x 10^{-10} AMPERES	PICOCOULOMBS
6.5	40	47
12	60	43
13	75	44
34	130	42
64	140	25

CCI DETECTOR RESPONSE TO 0.027% BUTANE IN AIR (**)

FLOW RATE IN CC/MINUTE	PEAK HEIGHT AT 4 x 10-10 AMPERES	PICOCOULOMBS
6.7	21	6.2
12	32	6.1

(*) Sample loop volume = 30 ml

(**) Sample loop volume = 15 ml

C. Linearity of Response With Sample Concentration

Figure VIII shows that the CCI detector is reasonably linear with the concentration of hydrocarbon sample diluted in air. The results in this Figure are reported for a filament current of 1.5 amperes and a flow rate of 12 ml per minute. At higher filament temperatures and/or lower flow rates the linear range of response to any hydrocarbons is generally increased, as would be expected from kinetic considerations.

D. Investigation of Interferences and Synergism

In order that the CCI detector might be used analytically for hydrocarbon determinations, it was necessary to ascertain that there would be no interferences from non-hydrocarbon components in typical auto exhausts and that the response to mixed hydrocarbons show non-synergistic effects.

It was experimentally determined that the CCID showed no significant response to the following components:

- Carbon Monoxide
- Hydrogen
- Carbon Dioxide
- Water
- Nitrogen*
- Oxygen
- Methane

A very limited test was made to check for the possibility of synergistic response of the CCID to mixtures of hydrocarbon. The data of Table II show that a one to one mixture of hexane and 2,2-DMB diluted in air produced an approximately additive response based on the radically different individual responses of hexane and 2,2-DMB. Further studies would be required to permit a conclusion that the detector is fully additive in an analytical sense; however, the results of this one test are encouraging in that no anomalous or synergistic effects were noted on a simple mixture.

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*Although it was not experimentally investigated it was believed there would be no response to the oxides of nitrogen since it is difficult to postulate ionic species which might be formed from these components in the reaction of the exhaust gas over the catalytic filament.

CCID RESPONSE
VS
% CONCENTRATION IN AIR

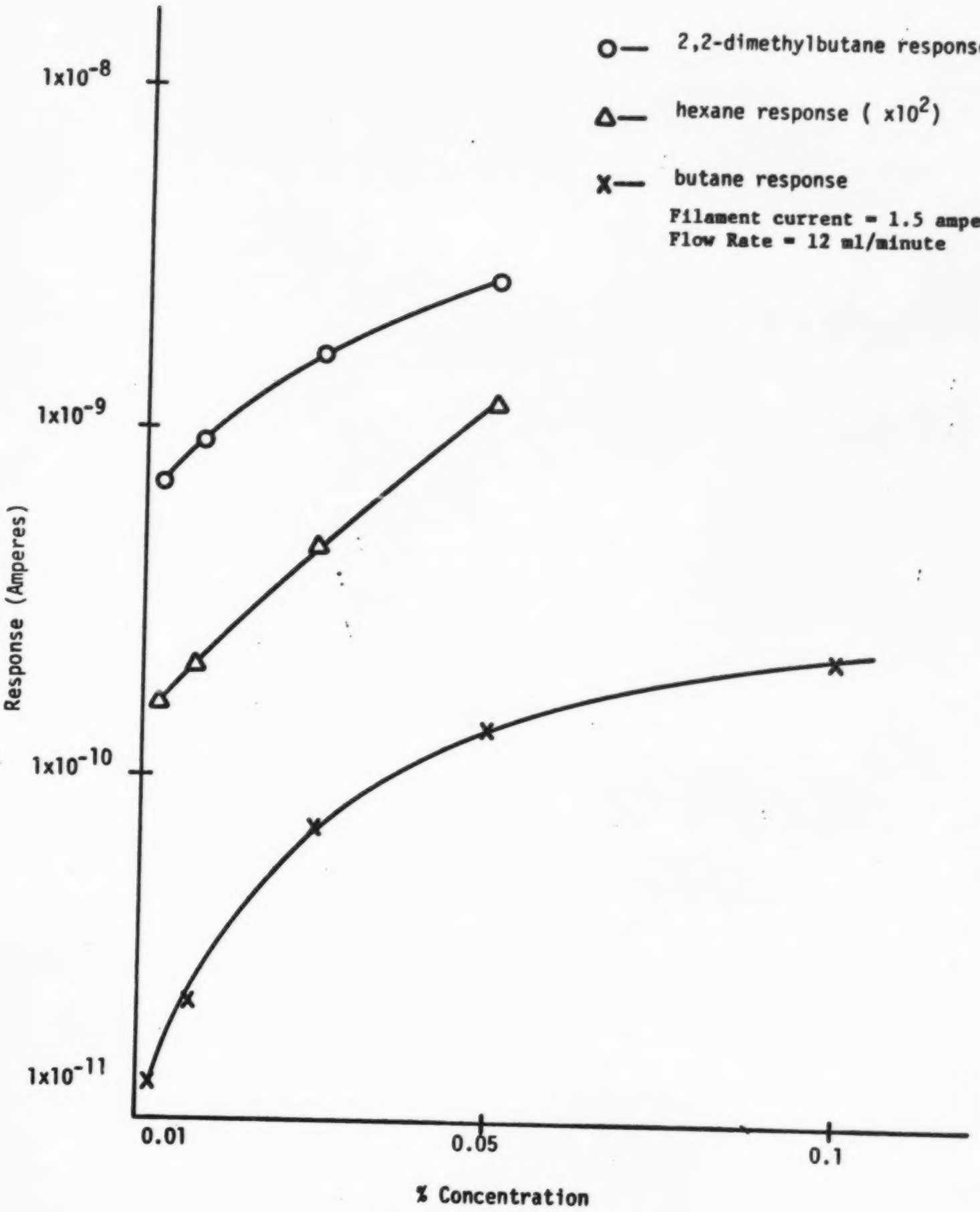

FIG. VIII

TABLE II

FID COMPARED TO CCID

SAMPLE (1) (2)	RELATIVE RESPONSE* Flame Ionization Detector (FID)	Catalytic Combustion Ionization Detector (CCID)
Butane	100	100
2,2-dimethylbutane	250	2700
Hexane	220	76
Benzene	250	1.14
Ethylene	220	0.72
Toluene	250	1.18
1:1 Mixture Hexane & 2,2-dimethylbutane	490	3025
Unleaded Amoco	250	570
Simulated Auto Exhaust	125	35.6

(1) Concentration of hydrocarbons fixed at 0.025% wt/wt basis in air, except for the 1:1 mixture of hexane and 2,2-dimethylbutane where their concentrations were adjusted to 0.025% each in the mixture.

(2) Methane and acetylene produced no measurable ion current in CCID.

* Response factors based on butane = 100

E. Comparison of CCID and FID Response

The FID (Flame Ionization Detector) is generally considered to provide a good measure of total hydrocarbon in auto exhaust in terms of total carbon present in the hydrocarbon fraction. Therefore, it is interesting to compare the responses of the CCID to the FID. Results are shown in Table II.

Under the conditions at which the FID and CCID devices were operated, the FID produced ion currents for N-butane-in-air samples approximately 5 to 10 times greater than the currents observed for the same N-butane samples with the CCID. The response to different types of samples for each detector is expressed relative to a N-butane value of 100.

Most noteworthy in Table II is the relatively high response of the CCID to branched compounds (2,2-DMB) and its relatively low response to aromatic compounds. No response was observed with the CCID on methane, and response to acetylene was negligible.

The heavy weighting of the presence of branched hydrocarbons and the absence of response to methane may be advantageous in a measurement designed to indicate the efficiency of a control device for reducing exhaust hydrocarbon emissions. It is obvious that extensive data must be obtained to correlate the CCID measurement with (1) exhaust control effectiveness, and (2) weighted potency of the pollutants emitted.

F. Tests on Actual Auto Exhausts

Table III shows results obtained from both FID and CCID measurements on actual auto exhaust samples from four different automobiles. The sampling procedure was described under Section I-B of this Report. During the sample taking the automobile engines were run at engine idle speed, approximately 1,000 rpm. In each test the automobiles had been operated to warm up the engines to normal conditions.

From the limited data of Table III it can be observed that the "best" and the "worst" cars were so identified by both the FID and CCID methods. It is interesting to note that the CCID magnified the response of both the "best" and the "worst" car.

The exhaust of the 1963 Sting Ray showed a surprisingly high CCID response. Subsequent discussions with the owner of this "hot" automobile revealed that the car was equipped with a cam shaft designed for racing. At idle speed this engine operated roughly and it was known that the valve action, optimized for high speed, allowed the intake and exhaust valves to be opened simultaneously for a brief period during engine idle or low speed operation. It is possible that the resulting blow-by of uncombusted high octane fuel would give

high concentrations of branched compounds in the exhaust gas. This would, of course, have accounted then for the very high CCID reading. Although the FID showed highest response to this same automobile, it did not magnify the effect since the FID would not emphasize the presence of branched hydrocarbons in the uncombusted fuel in the exhaust gas.

TABLE III

COMPARISON OF FID AND CCID RESPONSE ON ACTUAL AUTO EXHAUST SAMPLES

Sample From	FID RESPONSE		CCID RESPONSE	
	Peak Height	Amps Current $x10^{-10}$	Peak Height	Amps Current $x10^{-10}$
'66 Cutlass	1000	20	84	1.6
'63 Sting Ray	1400	24	240	4.6
'66 Mustang	400	8	8	0.32
'61 Corvette	900	18	18	1.0

III. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions have been drawn:

- **The catalytic combustion ionization technique may be employed as a means of measuring hydrocarbon in automobile exhaust gas.**

- **A relatively simple and reliable detector cell with replaceable catalytic filaments can be designed and fabricated.**

- **The pulse sampling method should be incorporated as an integral part of the CCID system. This will eliminate the need for critical flow adjustments and permit intermittent filament regeneration.**

- **A supporting electronics and meter read-out sub-system for the CCID and pulse sampling method can be engineered as a rugged, simple package. The total system would provide coulometric response.**

- **The CCID response to various hydrocarbons differs from that of the FID. However, the CCID may give a meaningful index measurement of hydrocarbon quantity and "quality" in auto exhaust.**

The following are recommendations:

- **A rugged, portable Auto Exhaust Gas Analyzer should be engineered. This single "black box" should provide for simultaneous and specific determinations of hydrocarbon and carbon monoxide. Under separate cover a proposal will be submitted by Micro Tek Instruments Corporation to undertake this activity.**

- **Several production prototype units of the Analyzer should be fabricated for field evaluation with regard to its reliability and simplicity of operation. Extensive data obtained on actual automobile exhaust samples should be correlated with other tests and analyses performed on the same samples.**